mechanism of the competitive formations of *n*-Bu and H radicals as noted above. In the *n*-BuMgBr reaction, on the other hand, reduction is more favored under more dilute conditions. The results suggest that the reduction takes place as a unimolecular decomposition of the ketone–Grignard reagent complex, while the addition occurs in higher order molecularity, as proposed by earlier studies.[7]

In conclusion, both organomagnesium and organolithium reagents react with benzophenone via an ET mechanism, but these reactions are different in the rate-determining steps and in the fates of the radical-ion pair formed via initial ET.

Experimental Section

Materials. Diethyl ether was dried over $LiAlH_4$ and distilled before use. Hexane was dried over CaH_2 and distilled. All glassware was flame-dried, and anhydrous solutions were handled under dry nitrogen by using Schlenk tube techniques.[8] Substituted benzophenones were prepared as described previously.[3a] *n*-BuLi was purchased from Merck (1.6 M, hexane soln). *n*-BuMgBr was prepared from *n*-BuBr (bp 101 °C) and doubly sublimed Mg (Ventron). These organometallic reagents were standardized by a method described in the literature.[9]

Reactions. All reactions were carried out at 0.0 ± 0.1 °C. The relative reactivities of the substituted benzophenones were determined as described before.[3a] The concentrations of the ketone and the reagent in this experiment were 0.07 M and 0.03 M, respectively. Reactions to determine the product ratio were carried out under various concentrations as noted in footnotes to Tables I and II. All substituted tertiary alcohols (1-aryl-1-phenylpentanols) were isolated from the reaction solution by using silica gel column chromatography. Substituted benzhydrols were obtained by the reactions of substituted benzophenones with $LiAlH_4$. The identity of these compounds was confirmed by ^1H NMR (Bruker-AM360) and IR (HITACHI 260-10) spectroscopy as well as melting points (where the literature values were available), and the purity was judged to be >98% by GLC (dibenzyl ether, internal standard). Product ratios were determined by GLC (PEG HT, 2 m) by calibrating detector response factors of these products. Material balance was confirmed for the parent benzophenone and found to be excellent (>98% for both reagents).

Acknowledgment. We are indebted to the Material Analysis Center of ISIR for the NMR measurements.

Supplementary Material Available: Relative reactivity data of benzophenones with *n*-BuMgBr and *n*-BuLi and the NMR and IR data and spectra of the products (15 pages). Ordering information is given on any current masthead page.

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Phenylazophenol–Quinone Phenylhydrazone Tautomerism in Chromogenic Cryptands and Corands with Inward-Facing Phenolic Units and Their Acyclic Analogues

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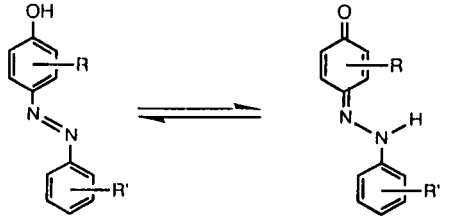
Received August 23, 1990

A series of 4-(4′-nitrophenol)azophenol compounds is prepared in which ether oxygen-containing substituents are attached at the 2- and 6-positions or connect the 2- and 6-positions to incorporate the chromophoric unit into corand or cryptand structures with inward-facing phenolic groups. The phenylazophenol–quinone phenylhydrazone tautomerism of these compounds, as probed by ultraviolet–visible spectroscopy, reveals a pronounced effect of the structure of the ether oxygen-containing substituents or bridging unit upon the tautomeric equilibrium. Chromogenic responses of five cryptands with inward-facing phenolic groups to sodium and potassium ions are determined and compared.

The tautomerism between *p*-arylazophenols 1 and *p*-quinone arylhydrazones 2 has been investigated extensively on compounds derived from phenols, anthranols, and particularly naphthols and summarized in several reviews.[3-10] On the basis of the results of early investigations, compounds from the phenol series were long assumed to exist in the azo form only. Later studies by ^1H NMR[11-13] and IR[14] spectroscopy revealed that introduction



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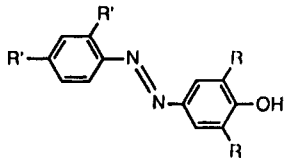
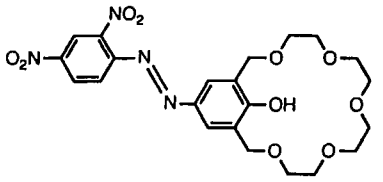
of strongly electron-withdrawing substituents on the phenyl ring and/or electron-donating alkyl groups on the phenol ring can markedly enhance the proportion of the *p*-quinone arylhydrazone tautomer. For example, the relative proportion of hydrazone tautomer for compounds **3–5** increases from 0 to 8 to 95%, respectively.[14,15]



	R	R'
3	H	H
4	H	NO_2
5	CH_3	NO_2
6	CH_2OCH_3	NO_2

Bridging of the 2- and 6-positions of 4-(2′,4′-dinitrophenyl)azophenol with a polyether chain produces chromogenic corand **7**, which has been used for the colorimetric



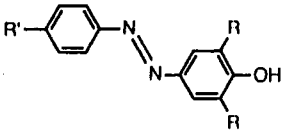
7

determination of lithium,[16] rubidium[17] and cesium.[17] Although the acyclic analogue **6** is reported to contain 40% of the hydrazone tautomer, corand **7** exists totally in the azo form.[18] This has been attributed to hydrogen bonding of the phenolic unit with ethereal oxygens to stabilize the azophenol structure of corand **7**.

To provide insight into the effect of structural variation within chromogenic corands and cryptands upon the *p*-phenylazophenol–*p*-quinone phenylhydrazone tautomerism, a series of 10 2,6-substituted 4-(4′-nitrophenyl)azophenol compounds has been synthesized and examined.

Results and Discussion

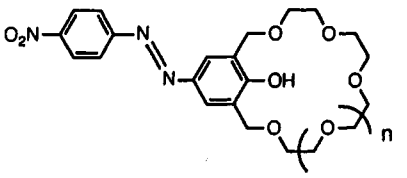
Synthesis. For the acyclic model compounds, coupling of commercially available 2,6-dimethoxyphenol with benzenediazonium chloride afforded azo dye **8**.[15] When a



	R	R'
8	OCH_3	H
9	OCH_3	NO_2
10	CH_2OCH_3	NO_2

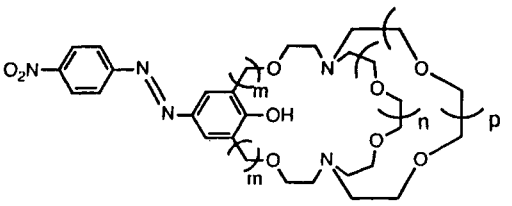
diazonium salt generated from *p*-nitroaniline was employed, model compound **9** was produced. Azo dye **10** was obtained by reaction of 2,6-bis(methoxymethyl)phenol with *p*-nitrobenzenediazonium chloride. The requisite phenol was prepared in 41% yield from the reaction of 2,6-bis(bromomethyl)phenyl acetate[19] and sodium methoxide.

Chromogenic corands **11** and **12** were prepared by coupling of the corresponding corand phenols[20] with *p*-nitrobenzenediazonium chloride in 67 and 60% yields, respectively.



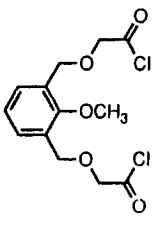
	n
11	1
12	2

Chromogenic cryptands **13–16** were synthesized by reaction of the corresponding cryptand phenols[21] with aqueous sodium hydroxide and then *p*-nitrobenzenediazonium tetrafluoroborate in yields of 20, 52, 54, and 57%, respectively.[22]

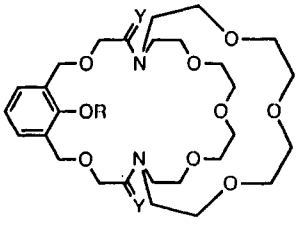


	m	n	p
13	0	1	0
14	0	1	1
15	0	2	1
16	0	2	2
17	1	2	2

Chromogenic cryptand **17** was prepared by a four-step reaction sequence. High-dilution cyclization of diacid chloride **18**[24] with 1,13-diaza-24-crown-8[25] gave cryptand



18



	R	Y
19	CH_3	O
20	Na	H_2

diamide **19** in 60% yield. Concomitant reduction and

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Table I. UV-Visible Spectral Characteristics (λ_{max}, nm and $\epsilon(\lambda_{max})$) and pK_a Values of Chromogenic Compounds 8–17 in 50% Aqueous Dioxane (v/v)

	HL[a]			
compd	azo form	hydrazone form	L^-[b]	pK_a[c]
8	375 (17550)		484 (28650)	10.1 ± 0.14
9		480 (33175)	594 (41910)	8.9 ± 0.07
10	380 (24980)		530 (35270)	8.2 ± 0.01
11	379 (25160)		532 (37800)	8.9 ± 0.1
12	380 (27510)		531 (39960)	8.7 ± 0.1
13	349 (4200)	493 (21000)	567 (13700)	ND[d]
14	383 (12140)	483 (22070)	588 (31000)	ND
15	391 (15100)	485 (12700)	596 (33650)	ND
16	397 (16500)	482 (16700)	594 (36000)	9.2 ± 0.2
17	380 (19740)		536 (30850)	9.0 ± 0.05

[a] HL is nonionized chromogenic compound in 0.1 M HCl. [b] L^- is fully ionized chromogenic compound in 0.1 M (TMA)OH. [c] Zwitterionic buffers were used in the determination; pK_a values are average of three determinations ± standard deviation. [d] Not determined.

demethylation of **19** with lithium aluminum hydride[21] produced cryptand phenolate **20**, which was coupled with *p*-nitrobenzenediazonium tetrafluoroborate to afford chromogenic cryptand **17** in 65% overall yield for the two steps.

The structures of azo dyes **8–17**, as well as intermediate **19**, were verified by ^{1}H NMR and IR spectra and by elemental analysis.

Phenylazophenol–Quinone Phenylhydrazone Tautomerism of Chromogenic Compounds 8–17. The UV-visible spectra of the nonionized (HL) forms of compounds **8–17** were taken in dioxane/0.2 M aqueous hydrochloric acid (1:1). Results are recorded in Table I.

For the mobile equilibrium between the azo form **1** and hydrazone form **2**, it has been established that the absorption for the latter is bathochromic compared with the former and has higher absorptivity.[15] Acyclic model compound **8** has been reported to exist exclusively in the azo form due to its stabilization by intramolecular hydrogen bonding.[15] Compound **8** is found to exhibit an absorption maximum at 375 nm (Table I). In sharp contrast, when a *p*-nitro group is introduced, compound **9** shows a single absorption maximum at 480 nm with a much higher molar absorptivity. In going from acyclic model compound **9** to **10**, a marked spectral change is observed once again and a single absorption maximum at 380 nm with a reduced molar absorptivity is noted for **10**.

These results are consistent with the existence of only the azo form for acyclic model compounds **8** and **10** and only the hydrazone form for **9** and reveal a high sensitivity of the *p*-phenylazophenol–*p*-quinone phenylhydrazone tautomeric equilibrium to substituent variation in this system. Thus, the addition of a strongly electron-withdrawing group to the phenyl ring of compound **8** produces a change from the azo form to the hydrazone form for **9**. Then, replacement of the methoxyl groups at the 2,6-positions of compound **9** with methoxymethyl groups causes a shift back to the azo form for **10**. The change between compounds **9** and **10** may be attributed to enhanced intramolecular hydrogen bonding of the phenolic group in **10** with the more basic dialkyl ether oxygens.

Chromogenic corands **11** and **12** exhibit single absorption maxima at 379 and 380 nm, respectively, which are consistent with the presence of only the azo tautomer. Chromogenic cryptand **17**, which is also related to the acyclic model compound **10**, shows a single absorption band with a maximum at 380 nm for the azo form. For chromogenic corands **11** and **12** and cryptand **17**, intramolecular hydrogen bonding of the phenolic group could conceivably involve various dialkyl ether oxygens of the bridging units.

In contrast with the results obtained for chromogenic cryptand **17**, two absorption maxima are observed in the UV-visible spectra for cryptands **13–16**, which demonstrates that both the azo and hydrazone forms are present. Since the only structural difference between chromogenic cryptands **16** and **17** is the presence of a methylene group spacer between the phenolic ring of the 4-(4′-nitrophenyl)azophenol chromophore and the first oxygen of the bridging unit in **17**, intramolecular hydrogen bonding of the phenolic group with that dialkyl ether oxygen atom in **17** must be important in stabilizing its azo form. Although a shift of the absorption maximum for the azo form to longer wavelengths and an increase of the molar absorptivity is apparent as the cavity size is increased for chromogenic cryptands **13–17**, there is no uniform trend in the values for the hydrazone form absorptions.

The pK_a values for azo dyes **8–12**, **16**, and **17** in 50% aqueous dioxane are listed in Table I. As would be anticipated, the pK_a value of 10.1 for compound **8**, which does not possess a *p*-nitro substituent, is considerably higher than those for compounds **9–12** and **17**, which are all in the range of 8.2–9.0. The pK_a values for the chromogenic cryptands **13–15** could not be determined accurately, presumably due to the presence of the tautomeric equilibria. An approximate pK_a value of 9.2 ± 0.2 was found for chromogenic cryptand **16**.

Spectral Properties of Ionized Forms for Chromogenic Compounds 8–17. The UV-visible spectra of the ionized (L^-) forms of **8–17** were measured in dioxane/0.2 M aqueous tetramethylammonium hydroxide (1:1). Results are recorded in Table I. It is interesting to note that with the 4-(4′-nitrophenyl)azophenol compounds **8**, **10–12**, and **17**, for which the nonionized compounds exist solely in the azo form, the absorption maxima for the ionized species are in the range of 530–536 nm. On the other hand, with **9** and **14–16**, for which the nonionized compounds are present either solely or partially in the hydrazone form, the absorption maxima for the ionized species occur at 588–596 nm. Presumably, this difference is produced by the change of first atom at the 2,6-positions from carbon in the former group to oxygen in the latter. The intermediate absorption maximum value and extraordinarily low molar absorptivity observed for **13** indicates only partial ionization of the phenolic group under these conditions due to stronger hydrogen bonding of the phenolic proton within the small cavity of the cryptand unit.

It has been reported in the patent literature[23] that the absorption maxima for the lithium, sodium, potassium, rubidium, and cesium phenolate forms of chromogenic cryptand **14** are 515, 510, 570, 567, and 500 nm, respectively. Since the conditions under which these measurements were performed are not specified, neither the pH nor the solvent composition for these measurements are known. Also, the ratio of metal ion to chromophore concentrations is unknown.

Due to our interest in the colorimetric determination of sodium and potassium in physiological fluids, responses

Table II. Sodium and Potassium Responses of Chromogenic Cryptand Phenols 13–17 at pH Optimum[a] in 50% Aqueous Dioxane (v/v)

compd	optimum pH	form	λ_{max}, nm	$\epsilon(\lambda_{max})$
13		NaL	513	10000
	10.0			
		KL	499	10000
14		NaL	502	18800
	11.0			
		KL	563	27800
15		NaL	529	22400
	11.0			
		KL	529	22250
16		NaL	561	34900
	10.0			
		KL	535	19800
17		NaL	519	28300
	10.0			
		KL	528	30950

[a] Buffers: pH 10.0, 0.1 M CHES; pH 11.0, 0.1 M CAPS.

of the five chromogenic cryptands 13–17 to the presence of 400-fold excesses of sodium ions and of potassium ions in 50% aqueous dioxane were determined. Absorption maxima and molar absorptivities at the pH optima are presented in Table II. (The pH optimum is defined as the pH at which the largest shift is observed between the absorption maxima for the sodium and potassium phenolates, NaL and KL, respectively.) Chromogenic cryptands 13, 15, and 17 show only slight differences in wavelength maxima and molar absorptivities between their NaL and KL forms at any pH and therefore are unsuitable as reagents for the colorimetric determintion of sodium or potassium ions. The lack of full ionization in 13 mentioned earlier is reflected in low absorptivities for the sodium and potassium responses.

At pH 11.0 for chromogenic cryptand 14, there is a 61-nm shift in the absorption maximum to longer wavelength and a substantially higher molar absorptivity for the KL form versus the NaL form. Somewhat unexpectedly for chromogenic cryptand 16, which should possess a much larger cryptand cavity, the NaL form exhibits the longer wavelength absorption than the KL form by 26 nm and an almost doubling of the molar absorptivity (Figure 1). Thus, chromogenic cryptands 14 and 16 exhibit potential for the colorimetric determination of potassium and sodium, respectively.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 267 spectrophotomer. ^{1}H NMR spectra were measured with Varian EM 360A and Gemini 200-MHz spectrometers, and chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. The UV-visible spectra were recorded on a Beckman DU-8 spectrophotometer. An Orion 601-A digital ion analyzer was used in the pH measurements. Elemental analysis was performed by Galbraith Laboratories of Knoxville, TN, and Spang Microanalytical Laboratory of Eagle Harbor, MI.

Materials. Unless specified otherwise, reagent-grade reactants and solvents were used as received from chemical suppliers. Benzene was dried over molecular sieves (4A). Tetrahydrofuran was distilled before use from sodium benzophenone ketyl. *p*-Nitrobenzenediazonium tetrafluoroborate was prepared according to a literature procedure.[26]

General Procedure for the Preparation of Model Compounds 8–10 and Chromogenic Corands 11 and 12. Aniline or *p*-nitroaniline (14.4 mmol) in 42 mL of 1 N HCl was treated with $NaNO_2$ (1.16 g, 16.8 mmol) at 0 °C. The resultant diazonium salt solution was added dropwise with vigorous stirring to a solution of the appropriate phenol (3.6 mmol) in 70 mL of 0.25 N NaOH. After 10 min, the yellow solution was made basic with 1 N NaOH, which produced a color change. The mixture was stirred overnight and then acidified with 6 N HCl. The precipitate was filtered and washed with water. The air-dried product was chromatographed on alumina with benzene/ethanol (10:1) as eluent.

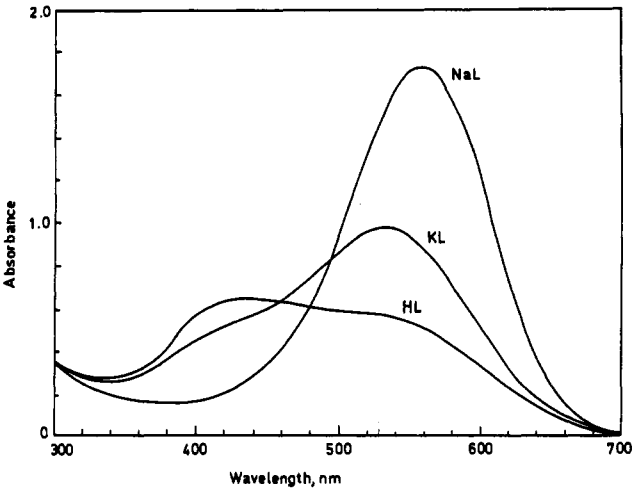

Figure 1. UV-visible spectra of sodium (NaL) and potassium (KL) response of chromogenic cryptand 16 (HL) in 50% aqueous dioxane at pH 10.0.

Model compound 8:[15] IR (deposit) 3300 (OH), 1450 (N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.97 (s, 6 H), 5.88 (s, 1 H), 7.29 (s, 2 H), 7.35–7.55 (m, 3 H), 7.86 (d, 2 H).

Model compound 9: red solid with mp 230–232.5 °C; IR (deposit) 3260 (NH), 1620 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 6 H), 5.97 (s, 1 H), 7.33 (d, 2 H), 8.16 (AB q, 4 H). Anal. Calcd for $C_{14}H_{13}N_3O_5$: C, 55.45; H, 4.32. Found: C, 55.41; H, 4.35.

Model compound 10: red crystals with mp 113–115 °C; IR (deposit) 3300 (OH), 1450 (N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.49 (s, 3 H), 4.68 (s, 4 H), 7.82 (s, 2 H), 7.95 (d, 2 H), 8.34 (d, 2 H), 8.52 (s, 1 H). Anal. Calcd for $C_{16}H_{17}N_3O_5$: C, 58.00; H, 5.17. Found: C, 58.04; H, 5.18.

Chromogenic corand 11: 67% yield of a black, amorphous solid with mp 68–70 °C; IR (deposit) 3330 (OH), 1130 and 1100 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.50–3.90 (m, 16 H), 4.73 (s, 4 H), 6.70 (br s, 1 H), 7.75–8.45 (m, 6 H). Anal. Calcd for $C_{22}H_{27}N_3O_8 \cdot 0.75H_2O$: C, 55.63; H, 6.04. Found: C, 55.73; H, 5.76.

Chromogenic corand 12: 60% yield of a red solid with mp 104–105 °C; IR (deposit) 3308 (OH), 1105 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.45–4.05 (m, 20 H), 4.75 (s, 4 H), 7.70–8.40 (m, 7 H). Anal. Calcd for $C_{24}H_{31}N_3O_9$: C, 57.02; H, 6.18. Found: C, 56.78; H. 6.09.

2,6-Bis(methoxymethyl)phenol. Sodium methoxide (1.19 g, 22.0 mmol) was added to a solution of 2,6-bis(bromomethyl)-phenyl acetate[19] (3.22 g, 10.0 mmol) in dry THF (30 mL) at 0–5 °C. The mixture was stirred for 1 h at room temperature and then refluxed overnight. Methanol (10 mL) was added, the mixture was stirred for 2 h, and the solvent was removed in vacuo. Ethyl acetate (30 mL) was added to the residue, and the insoluble material was filtered and washed with ethyl acetate. Evaporation of the solvent in vacuo gave a violet glass that was partitioned between $CHCl_3$ (20 mL) and 6 N HCl (10 mL). Drying ($MgSO_4$) and evaporation of the organic layer in vacuo afforded 0.75 g (41%) of the title compound as a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 3.42 (s, 6 H), 4.58 (s, 4 H), 6.82 (t, 1 H), 7.10 (d, 2 H), 7.79 (s, 1 H). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.60; H, 8.02.

General Procedure for the Preparation of Chromogenic Cryptands 13–17. Aqueous 32% NaOH was added to the cryptand phenol (2.2 mmol) until the solution was basic. The brown solution was evaporated to dryness in vacuo, and glacial acetic acid (20 mL) was added to give a clear yellow solution that

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was cooled to 0 °C. To the vigorously stirred solution was added dropwise a solution of *p*-nitrobenzenediazonium tetrafluoroborate[26] (0.59 g, 2.5 mmol) in water (30 mL). The mixture was stirred overnight at room temperature and evaporated to dryness in vacuo. The residue was extracted repeatedly with toluene, and the combined extracts were washed several times with deionized water and dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was purified by chromatography on basic alumina with chloroform and chloroform/ethanol as eluents.

Chromogenic cryptand 13: 20% yield of a dark red semisolid; IR (film) 3354 (OH), 1095 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30–3.00 (m, 12 H), 3.20–3.60 (m, 16 H), 6.67 (s, 2 H), 8.15 (AB q, 4 H), 8.60 (br s, 1 H). Anal. Calcd for $C_{26}H_{35}N_5O_8$: C, 57.24; H, 6.47. Found: C, 57.01; H, 6.63.

Chromogenic cryptand 14:[22] 48% yield of a red-brown semisolid; IR (neat) 3350 (OH), 1100 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.70–3.10 (m, 12 H), 3.50–3.90 (m, 16 H), 4.10–4.40 (m, 4 H), 7.42 (s, 2 H), 7.80–8.50 (m, 5 H). Anal. Calcd for $C_{28}H_{39}N_5O_9 \cdot H_2O$: C, 55.34; H, 6.80. Found: C, 55.20; H, 6.95.

Chromogenic cryptand 15: 54% yield of a dark red oil; IR (film) 3352 (OH), 1100 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60–3.20 (m, 12 H), 3.35–4.40 (m, 24 H), 6.65 (s, 1 H), 7.40 (s, 2 H), 8.13 (AB q, 4 H). Anal. Calcd for $C_{30}H_{43}N_5O_{10} \cdot H_2O$: C, 55.29; H, 6.96. Found: C, 55.45; H, 7.18.

Chromogenic cryptand 16: 57% yield of a red-brown semisolid; IR (film) 3358 (OH), 1107 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30–3.10 (m, 12 H), 3.20–3.90 (m, 28 H), 7.20–7.45 (m, 3 H), 8.15 (AB q, 4 H). Anal. Calcd for $C_{32}H_{47}N_5O_{11}$: C, 56.71; H, 6.99. Found: C, 56.54; H, 7.00.

Chromogenic cryptand 17: 65% yield of a red-brown glass; IR (film) 3400 (OH), 1135 and 1105 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.70–2.95 (m 12 H), 3.45–3.80 (m, 28 H), 4.69 (s, 4 H), 4.85 (br s, 1 H), 7.86 (s, 2 H), 8.13 (AB q, 4 H). Anal. Calcd for $C_{34}H_{51}N_5O_{11}$: C, 57.86, H, 7.28. Found: C, 57.74; H, 7.31.

Cryptand Diamide 19. Under argon, a solution (64 mL) of diacid chloride 18[24] (1.61 g, 5.00 mmol) in dry benzene and a solution (64 mL) of 1,13-diaza-24-crown-8[25] (1.75 g, 5.00 mmol) and triethylamine (1.88 mL, 13.6 mmol) in benzene were added simultaneously with two syringe pumps to 150 mL of vigorously stirred benzene at room temperature during 12 h. The reaction mixture was stirred overnight, the solvent was removed in vacuo, and the residue was chromatographed on alumina with chloroform/ethanol (49:1) as eluent to give diamide **19** (1.80 g, 60%) as a white, waxlike solid with mp 78–80 °C: IR (film) 1645 (C=O), 1110 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.30–3.85 (m, 30 H), 3.68 (s, 3 H), 4.00–4.20 (m, 6 H), 4.66 (AB q, 4 H), 7.12 (t, 1 H), 7.40 (d, 2 H). Anal. Calcd for $C_{29}H_{46}N_2O_{11} \cdot 0.5CHCl_3$: C, 53.82; H, 7.12. Found: C, 54.11; H, 6.88.

Cryptand Sodium Phenolate 20. A solution of diamide **19** (1.25 g, 2.10 mmol) in dry THF (15 mL) was added to a suspension of $LiAlH_4$ (0.66 g, 17.5 mmol) in THF (65 mL). The mixture was refluxed for 20 h and cooled and 5% aqueous NaOH was added. The inorganic solid was filtered and washed several times with THF. The solvent was removed in vacuo to afford 0.85 g (73%) of **20** as a pale green foam that was directly used in the preparation of **17** without additional purification.

UV-Visible Spectroscopic Properties of Chromogenic Compounds 8–17 and Determination of Their pK_a Values. Chromogenic compounds **8–17** were dissolved in dioxane to make stock solutions of 1.0×10^{-4} M. Solutions were made from 1.0 mL of the stock solution and 1.0 mL of 0.2 M HCl for the nonionized form (HL) and from 1.0 mL of the stock solution and 1.0 mL of 0.2 M tetramethylammonium hydroxide for the ionized form (L^-) and were scanned in a 1-cm pathlength cuvette from 700 to 300 nm with a Beckman DU-8 spectrophotometer. Molar absorptivities (ϵ) at wavelength maxima (λ_{max}) were calculated according to Beer's law.

For the pK_a determinations, absorbances were measured at the acid and base wavelength maxima of the chromogenic compounds in a zwitterionic buffer ((cyclohexylamino)ethanesulfonic acid (CHES)) at pH values equal to the pK_a and the p$K_a \pm 0.5$ units.

Responses to Sodium and Potassium. The reagents for obtaining sodium and potassium responses consisted of 5.0×10^{-5} M chromogenic compound in 50% (v/v) dioxane/water and an appropriate buffer (see Table II). Final concentration of sodium or potassium ions in each cuvette was 2×10^{-2} M.

Notes

Unimportance of Steric Effects in Controlling the Stereochemistry of Base-Promoted, 1,2-Eliminations from *exo*-2-Bicyclo[2.2.1]heptyl Tosylate and Closely Related Compounds

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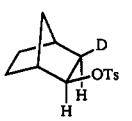
Received May 30, 1990

Greater facility of reactions involving the exo faces of bicyclo[2.2.1]heptyl compounds is usually attributed to greater steric hindrance by the 5,6-endo hydrogens to approach of the endo face than by the 7-syn hydrogen for exo attack.[3,4] Hydroboration, epoxidation, and many other reactions have been shown to be very sensitive to structural changes in this bicyclic ring system. For example, hydroboration of bicyclo[2.2.1]hept-2-ene gives solely the syn-exo adduct in contrast to only 22% of syn-exo addition for 7,7-dimethylbicyclo[2.2.1]hept-2-ene.[4]

The stereochemistry of base-promoted 1,2-elimination from bicyclo[2.2.1]heptyl compounds might be expected to be influenced by steric factors also.[3] As the base becomes bulkier, elimination involving base attack from the exo face should be accentuated. However, we have shown that the steric bulk of the base does not influence the level of preference for syn-exo 1,2-elimination from *exo*-3-deuterio-*exo*-2-bicyclo[2.2.1]heptyl tosylate (**1**) and chloride (**2**).[5] When the base was changed from potassium *tert*-butoxide to tri-2-norbornylmethoxide for reaction of **1** in triglyme (triethylene glycol dimethyl ether) in the presence of 18-crown-6, the percentage of syn-exo elimination ac-



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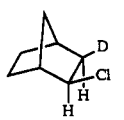

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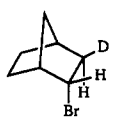

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